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14. ABSTRACT Molecular simulations were conducted to develop a better understanding of the structure-property relations for ionic liquids. A number of force fields were developed and applied to simulate several energetic ionic liquids as well as conventional ionic liquids. Mixture liquid properties were computed, simulations were conducted in the gas phase and melting points and crystal polymorph stability was simulated. Several new simulation techniques were developed to enable these calculations to be performed.				
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# **Final Progress Report for “Determination of Physical Properties of Ionic Liquids Using Molecular Simulations”**

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## **1. Objectives**

There were four main objectives in the project: 1) develop and refine classical force fields for modeling the solid and liquid phases of a range of ionic liquids; 2) use these force fields to compute thermodynamic and dynamic properties of ionic liquids in the condensed phase; 3) develop new simulation methods that can enable property calculations to be performed (at all or more efficiently); 4) systematically study how the structure and composition of the different ionic liquids affects the thermodynamic and transport properties of ionic liquids, and communicate these findings to synthetic groups.

## **2. Status of Effort – Executive Summary**

Objective 1: New force fields were developed for the following molecular compounds: hydrazine, monomethylhydrazine and unsymmetrical dimethyl hydrazine. Force fields were also developed for the following ionic liquids: 1-ethyl-3-methylimidazolium ethylsulfate, 1-ethyl-3-methylimidazolium butanesulfonate, 1-ethyl-3-methylimidazolium tricyanomethanide, hydrazinium nitrate, methylhydrazinium nitrate, unsymmetrical dimethylhydrazinium nitrate and 2-hydroxyethylhydrazinium nitrate. As part of a study on melting points, force fields were developed for sodium nitrate, lithium nitrate and potassium nitrate. Finally, a set of scripting tools was created that enables the generation of new ionic liquid force fields much faster than was possible before.

Objective 2: Using these force fields, pure liquid properties were computed, including density, coefficient of thermal expansion, isothermal compressibility, cohesive energy density, vapor pressure, vapor-liquid coexistence curves, critical points, and fluid structure. The solubility of several gases in ionic liquids were computed, as were the melting points and crystal polymorph stability of one particular ionic liquid.

Objective 3: A new Monte Carlo method called continuous fractional component Monte Carlo (CFC MC) was developed and implemented in three new open ensembles. It was used to compute pure and mixed gas solubility in ionic liquids. The pseudo-supercritical path sampling approach was refined for melting point and polymorph stability calculations. It was applied it to the calculation of the melting point of an ionic liquid. Finally, a new procedure was developed for computing the solubility limit of crystalline materials in liquid solvents. It was tested and validated on sodium chloride solubility in water and light alcohols.

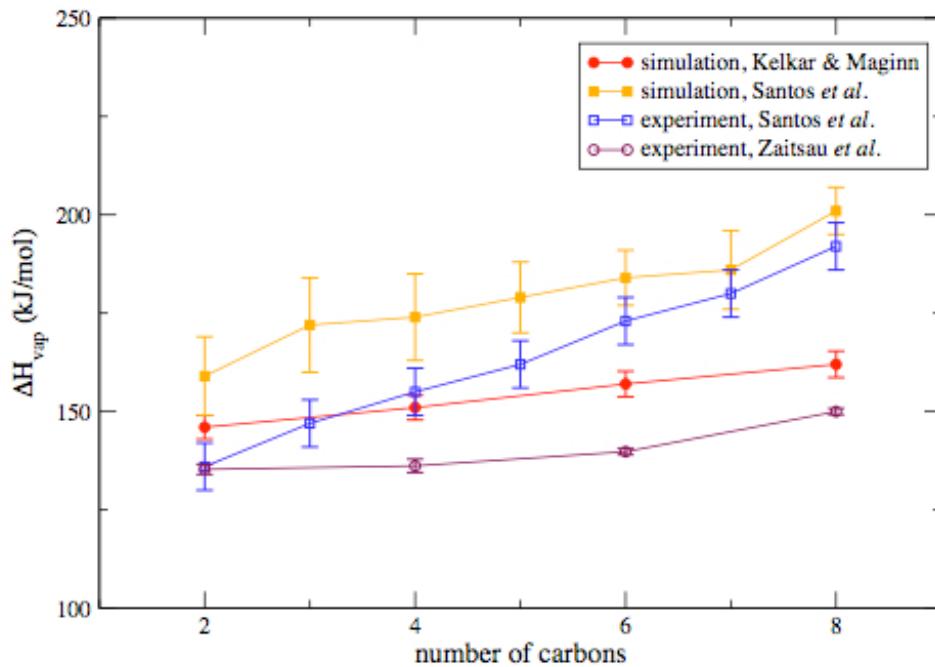
Objective 4: It was shown how hydrogen bonding between water and the anion of different ionic liquids slows the dynamics and can contribute to higher than expected viscosities. The liquid structure of the energetic ionic liquid 2-hydroxyethylhydrazinium nitrate was examined. It was shown that hydrogen bonding networks form that result in the low mobility of this ionic liquid. A combined experimental and simulation study was carried out to investigate the nature of ionic liquids in the vapor phase. It was determined that the most stable gas phase entities of ionic liquids are ion pairs. Studies to examine

the nature of the products that form when ionic liquids are subjected to strong electric fields, as occurs in electrospray experiments, were initiated.

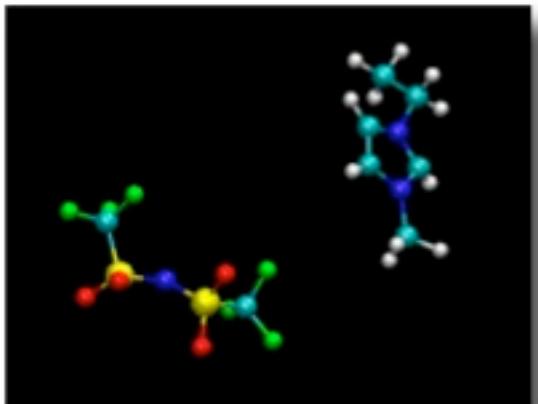
### 3. Accomplishments / New Findings

#### 3.1 Ionic Liquids in the Vapor Phase

A series of simulations were carried out to investigate the nature of ionic liquids in the vapor phase. The enthalpy of vaporization of different sized clusters (both neutral and charged) was computed. It was shown that by far the most energetically favorable species in the gas phase is a single ion pair that forms a neutral cluster [1]. Simulations in support of the experimental measurements of gas phase clusters in Prof. Stephen Leone's group were also carried out[2]. Based on the experiments and calculations, it was conclusively shown that normal vaporization of ionic liquids takes place by neutral clusters of a single cation and anion leaving the liquid phase.



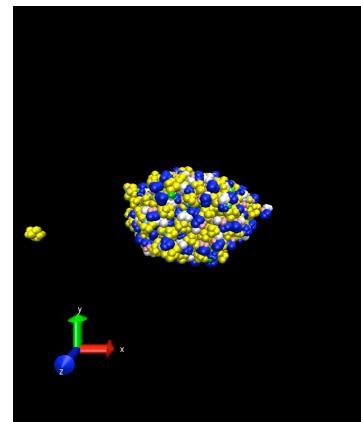
*Figure 1: Calculated and experimental enthalpy of vaporization for 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids as a function of the length of the alkyl group. Despite the scatter in the experimental data, the simulations appear to do a good job capturing both the magnitude and trend in the data.*



*Figure 2: Structure of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.*

Toward the end of the project, the behavior of ionic liquid droplets in vacuum with and without the presence of external electric fields were examined. For these simulations the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[\text{emim}][\text{Tf}_2\text{N}]$ ) was studied. This ionic liquid was chosen because it has been studied experimentally a great deal by collaborators Y. Chiu and co-workers at Hanscom Air Force Base. Figure 3 shows a snapshot from one of these simulations. It has been found that for this ionic liquid, a critical field strength of about 1 V/nm is required to observe emission, in good agreement with experimental field strengths.

The simulations enabled the calculation of the distribution of ions as a function of field strength and droplet size. Above a droplet size of about 25 ion pairs, the critical field strength for emission is independent of droplet size.



*Figure 3: Droplet of  $[\text{emim}][\text{Tf}_2\text{N}]$  in an electric field. Notice the emission of an ion on the left side of the droplet.*

### 3.2 Solubility and Dynamics of Ionic Liquids with Water

A series of studies were conducted to compute the solubility of water in ionic liquids and to see how water affects the properties of ionic liquids. All ionic liquids absorb water to some extent, and so it is critical to know both how much water is absorbed and how the properties are altered by water. Using the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (shown in Figure 2) the isotherm of water at 298 K was computed. Figure 4 shows the result. The only experimental data available was the saturation amount of water, and as can be seen the simulation results are consistent with the experiment. To perform the simulations, a new Monte Carlo procedure was developed (see section 3.3).

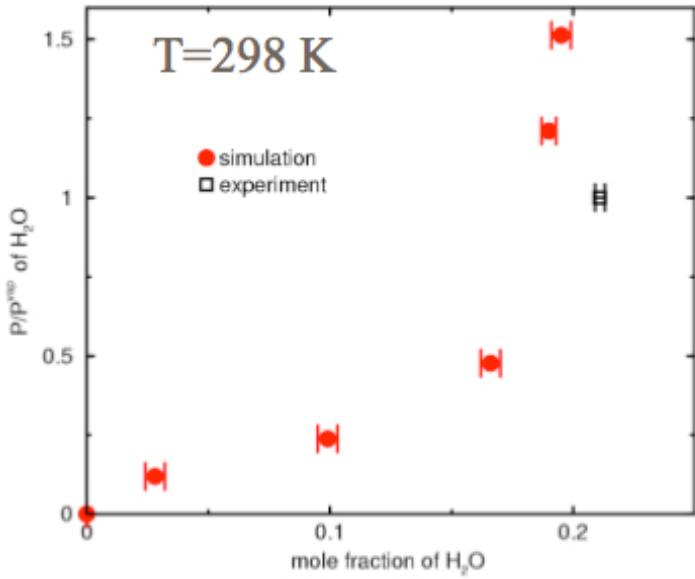
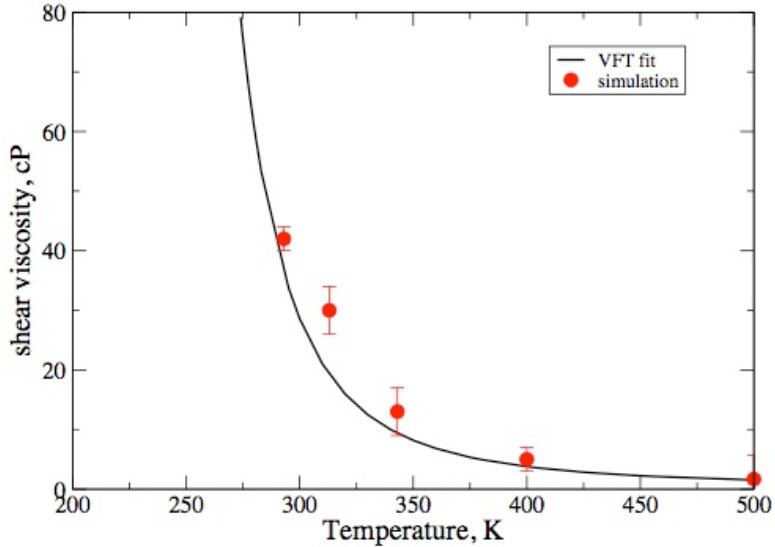


Figure 4: Computed water isotherm in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The black open symbol is the only experimental data point available. From ref. [3].

It has been claimed previously that neglect of polarizability leads to inaccuracies in the computed transport properties of ionic liquids such as viscosities and diffusivities. No doubt polarizability does yield greater mobility, but it was hypothesized that the consistently low viscosity that had been observed by many previous researchers was due more to the way in which they computed the viscosity than to anything having to deal with the force field. That is, most groups rely on relatively short (100-500 ps) simulations and evaluate the viscosity via conventional Green-Kubo integration. In this work it was shown that relevant relaxation times are *much* longer than these simulations, and so the dynamics being computed from a short simulation may be only local and not global. Thus, a proper simulation should be for longer than the longest relevant relaxation process. To overcome this, the reverse nonequilibrium molecular dynamics (RNEMD) procedure was utilized to compute the viscosities of ionic liquids. Figure 5 shows how calculations match experiments. Note that, even with a fixed charge model, the agreement between experiment and simulation is excellent.



*Figure 5: Computed viscosity as a function of temperature for 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The black line is a VFT fit to a large number of experimental data [3].*

Self-diffusivities were also computed, and these are shown in Figure 6. The computed dynamics are about a factor of two slower than the NMR results of Vasenkov et al., which is consistent with the slightly higher computed viscosity observed in Figure 5. The trend with temperature is captured well, as is the curious result that the larger cation has a larger self-diffusivity than the smaller anion.

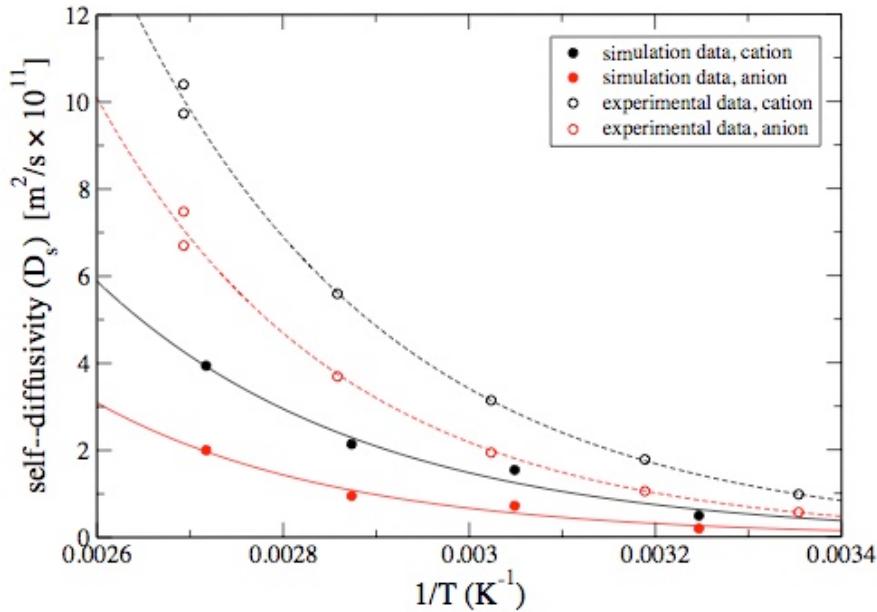


Figure 6: Computed self-diffusivity for 1-ethyl-3-methylimidazolium cation and bis(trifluoromethylsulfonyl)imide anion as a function of temperature. From ref [13].

### 3.3 New Simulation Methods

Three new simulation methods were developed and applied to compute properties of ionic liquids. The first method, called continuous fractional component Monte Carlo (CFC MC) enables efficient transfer of molecules between systems in open ensemble Monte Carlo. The method was described in references 4 and 8, and applied to compute CO<sub>2</sub> solubility in an ionic liquid in reference 7. Figure 4 shows water solubility results computed with this method, while Figure 7 shows a comparison between calculated and experimental isotherms for CO<sub>2</sub> and 1-n-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Agreement is quantitative in both cases.

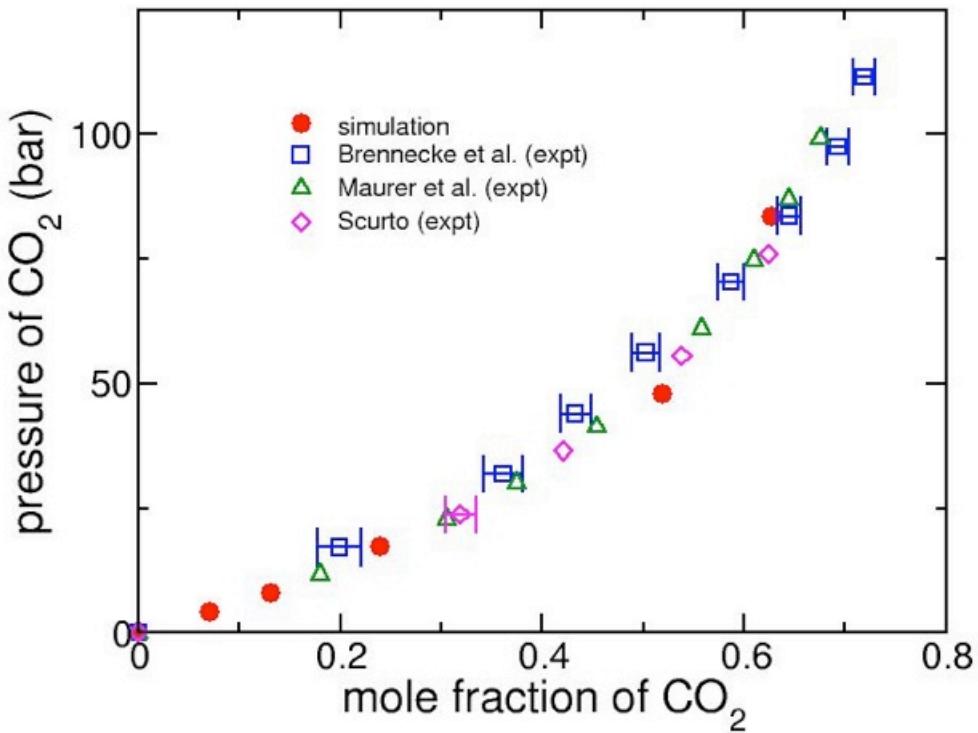


Figure 7: Calculated (red circles) and experimental (open symbols) solubility of CO<sub>2</sub> in the ionic liquid 1-n-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at 323 K. From ref. [7].

The method has been implemented in the osmotic and grand ensembles [4] as well as the Gibbs ensemble [8]. The method is being implemented in an open-source Monte Carlo code in order to make it more widely available to the broader research community.

The second new simulation method of this project was a refinement of an earlier technique called pseudosupercritical path sampling (PSPS). This method enables one to compute melting points and polymorph stability. The method works as follows. Relative free energy curves for a crystal and the liquid phase of the same substance are computed by conducting isotherm-isobaric simulations of both phases. The temperature-dependence of the enthalpy is computed and the relative free energies are obtained using the Gibbs-Helmholtz equation. Note that this gives the free energy of the solid and liquid phases relative to some unknown integration constant. As an example, Figure 8 shows such a construction for the ionic liquid 1-n-butyl-3-methylimidazolium chloride.

The next step is to determine the constants for the two phases and in so doing, obtain the free energies of both phases as a function of temperature. When the two are equal, the system is in coexistence. To do this, a thermodynamic cycle is constructed between the two phases at a given temperature.

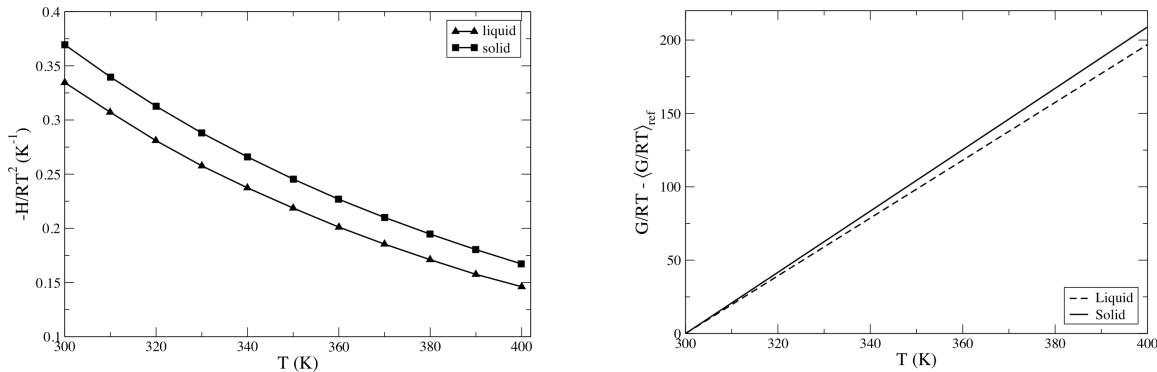


Figure 8: (left)  $-H/RT^2$  for the liquid and crystal phases of 1-n-butyl-3-methylimidazolium chloride. (right) The solid and liquid free energies using a reference state at 300K.

A schematic of the cycle is shown in Figure 9.

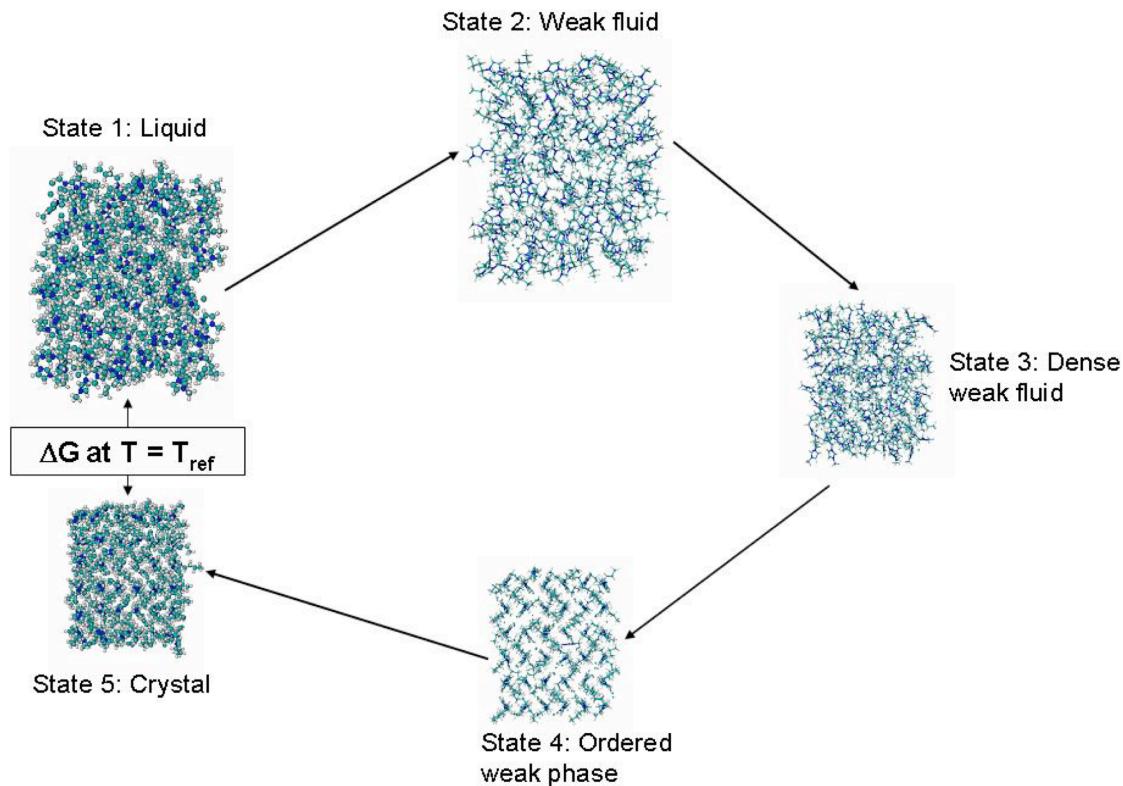
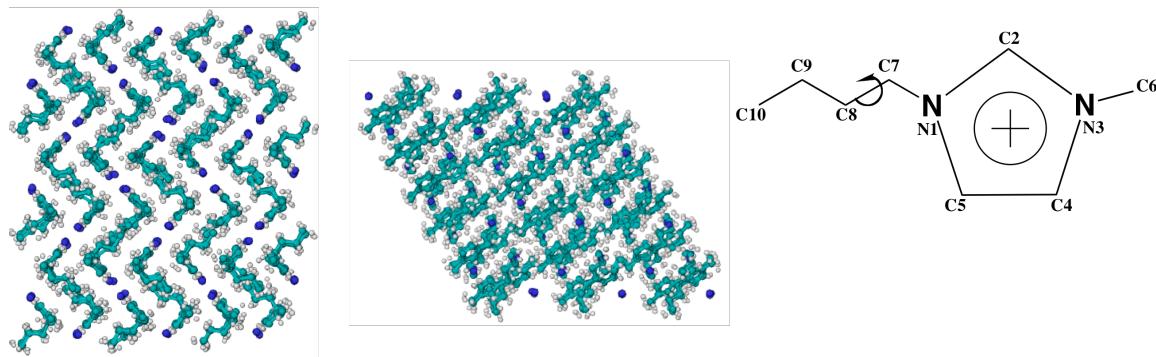


Figure 9: Thermodynamic cycle for determining the free energy difference between a crystal and a liquid at a given temperature.

In going from state 1 to state 2, a liquid is taken to a weakly interacting liquid by scaling the intermolecular energy between atoms. From state 2 to state 3, the density of the weakly interacting fluid is adjusted to yield the crystal density. State 4 is formed by using tethering potentials that order the fluid into the position found in a crystal. Finally, state 5 (the crystal phase) is recovered by turning back on the intermolecular interactions and

removing the tethering potential. At each step the free energy change is computed via thermodynamic integration. The result is the actual free energy difference between the liquid and crystal at a particular temperature. Given this difference at one temperature, the difference between the integration constants for the two phases are known, and the curves in Figure 8 can be shifted to find the coexistence temperature.

The PSPS method was used to conduct the first rigorous, free energy-based calculation of the melting point of an ionic liquid, and the first calculation in which the thermodynamic stability of two ionic liquid crystal polymorphs were computed [6]. Figure 10 shows two different polymorphs of 1-n-butyl-3-methylidazolium chloride.



*Figure 10: Orthorhombic (left) and monoclinic (middle) structures of the 1-n-butyl-3-methylidazolium chloride ( $[bmim]Cl$ ) ionic liquid. The  $bmim$  cation is shown on the right. The only difference between these two ionic liquids is the torsion angle about the C7 and C8 carbons.*

The table below shows the results of the calculations.

polymorph	$T_m^{expt}$ (K)	$T_m^{CLP}$ (K)	$T_m^{CMJJ}$ (K)	$\Delta H_{fus}^{expt}$ (kJ/mol)	$\Delta H_{fus}^{CLP}$ (kJ/mol)	$\Delta H_{fus}^{CMJJ}$ (kJ/mol)
orthorhombic	337-339	$302 \pm 5$	$308 \pm 9$	18.5-21.5	$26 \pm 3$	$19 \pm 4$
monoclinic	318-340	NA	$333 \pm 6$	9.3-14.5	NA	$23 \pm 3$

The “CLP” results are those obtained using a force field from Canongia-Lopes and Padua, while the “CMJJ” is the potential developed in this work. The CLP force field did not yield a stable monoclinic crystal. The CMJJ force field does a good job matching the melting points and heats of fusion.

The method was then applied to compute the melting points of  $\text{LiNO}_3$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  [17]. These systems were chosen because there experimental data for them and they make a good system to test the method on. Figure 11 shows the free energy difference between the crystal phase and liquid phase as a function of temperature for  $\text{LiNO}_3$ . The computed melting point is 459 K while the experimental value is 531 K. The difference is due to inaccuracies in the force field, though it is clear from how flat the curve is in Figure 11 that differences in free energy of a few kJ/mol can result in differences in melting points of 10s of degrees. This points out how difficult it is to get very accurate melting points.

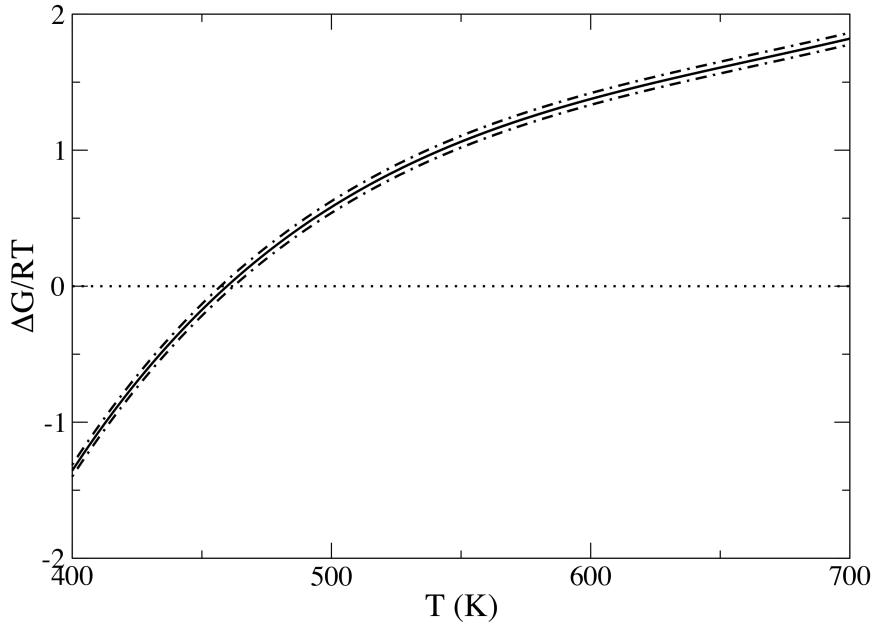
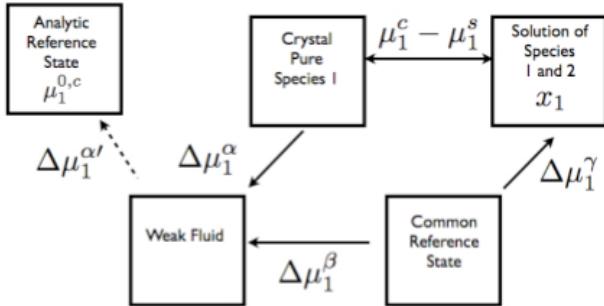


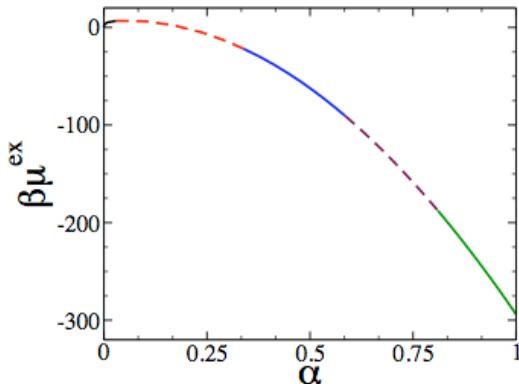
Figure 11: Computed free energy difference between the crystal and liquid phases of  $\text{LiNO}_3$ .

The third method developed in this project builds on the PSPS method and was used to compute the solubility limit of crystals in liquids [18]. Figure 12 shows a schematic of how the method works, where species 1 is the crystalline solute and species 2 is the liquid solvent. In this case, the PSPS method is used to compute the difference in chemical potential between the crystalline phase and a weakly interacting fluid phase ( $\Delta\mu^{\alpha}_1$ ). Expanded ensemble methods are used to compute the chemical potential difference between the crystalline species 1 in a common reference state (typically an ideal gas) and the weak fluid ( $\Delta\mu^{\beta}_1$ ). In addition, the chemical potential difference ( $\Delta\mu^{\gamma}_1$ ) is computed, which corresponds to the chemical potential difference between the solute in the common reference state and in solution at a given concentration. Figure 13 shows a typical result for sodium chloride in water. Note the huge free energy difference between the reference state and the solution phase. This gives an indication of how difficult it is to determine free energies of salts in aqueous solutions. The only way this calculation was possible was to break up the simulation into five “windows” where different parts of the potential were “turned on” at different times. In addition, advanced biasing methods were used to improve the transitions between adjacent states in the expanded ensemble [18].

By computing this quantity for a series of different solute concentrations, one can close the thermodynamic cycle in Figure 12 and determine the concentration that corresponds to coexistence. The temperature dependence can be incorporated by repeating the calculation at different temperatures. Figure 13 shows an example of one such calculation.



*Figure 12: A schematic of the method to determine the solubility limit of crystalline materials. The chemical potential of both phases is determined relative to a common reference state, such that relative (and not absolute) chemical potentials are required.*



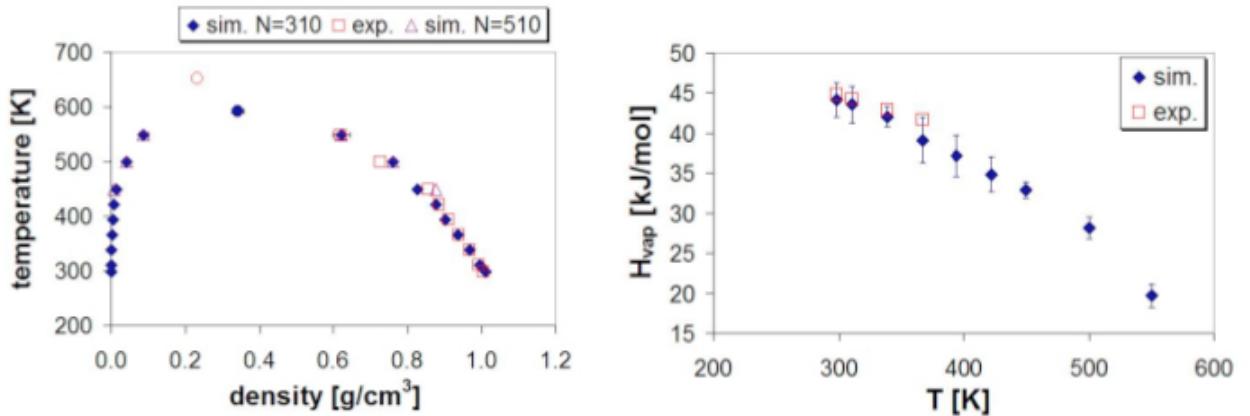
*Figure 13: Excess chemical potential of sodium chloride in water at 0.21M as a function of the coupling parameter. Different line colors and types are used to distinguish between the results of the five sampling windows used.*

### 3.4 Simulations of Energetic Ionic Liquids

A wide range of simulations on ionic liquids based on the hydrazinium cation paired with the nitrate anion were carried out [11]. Hydrazinium nitrate ( $[N_2H_5][NO_3]$ ), monomethylhydrazinium nitrate ( $[CH_3N_2H_4][NO_3]$ ), and unsymmetrical dimethylhydrazinium nitrate ( $[(CH_3)_2N_2H_3][NO_3]$ ) have melting points below 100°C, and thus may be considered as ionic liquids.

To start with, force fields for molecular hydrazine-like compounds were developed. The phase behavior of these compounds was computed using Gibbs ensemble Monte Carlo.

Figure 14 shows the computed and experimental vapor-liquid coexistence curve for hydrazine (left) and enthalpy of vaporization (right). Agreement with experiment is excellent.



*Figure 14: Computed and experimental vapor-liquid coexistence curve for hydrazine (left) and the associated enthalpy of vaporization as a function of temperature (right). Simulation results are in quantitative agreement with experiments.*

The Lennard-Jones force field parameters for these molecular species were then transferred to the ionic liquid analogues, and a range of properties were computed for the ionic liquids. Initially, simulations of the crystal phases of the ionic liquids were carried out. Figure 15 shows the results.

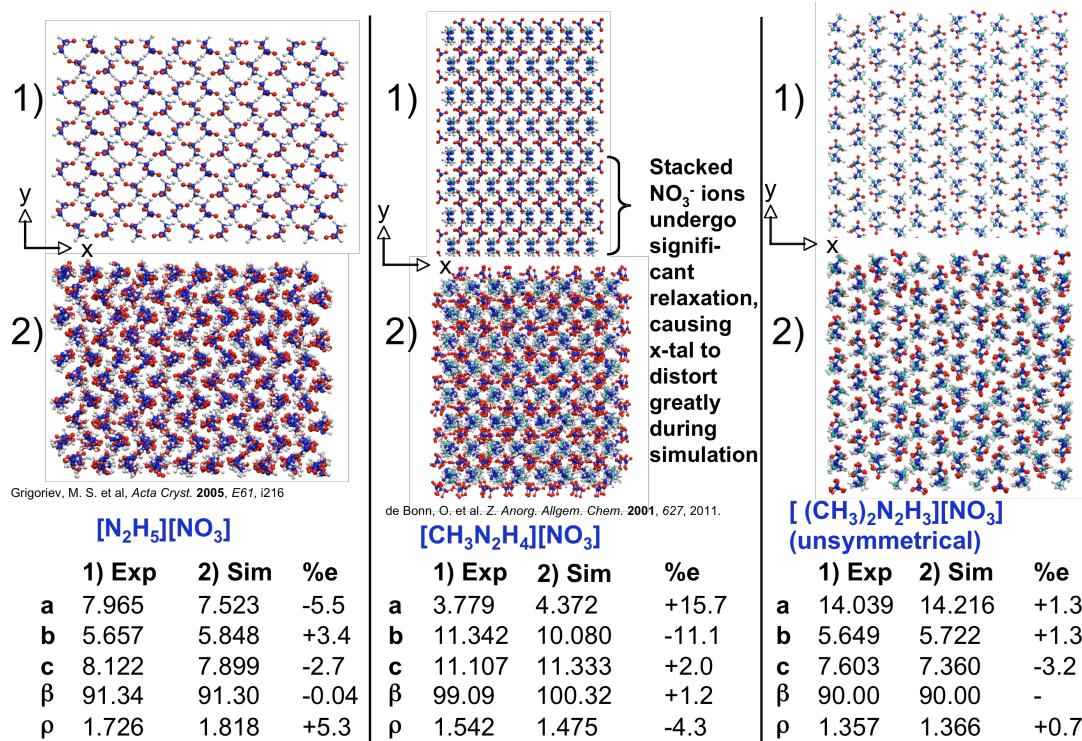


Figure 15: Simulated crystal phases of (from left to right): hydrazinium nitrate, monomethylhydrazinium nitrate and unsymmetrical dimethylhydrazinium nitrate.

The simulated monoclinic [N<sub>2</sub>H<sub>5</sub>][NO<sub>3</sub>] (Figure 15, left) shows moderate distortion compared to the x-ray lattice structure. Although the zig-zag pattern along the **a**-axis direction is maintained, there are considerable thermal fluctuations. The lattice contracts in the **a** and **c** directions by 5.5 and 2.9%, respectively, and contracts in the **b** direction by 3.5%. The  $\beta$  angle is in very good agreement with the experimental angle, differing by only 0.04%. Overall, despite the distortion in the cell, the simulated density is only 5.2% greater than the experimental value and agrees reasonably well.

The simulated lattice for [CH<sub>3</sub>N<sub>2</sub>H<sub>4</sub>][NO<sub>3</sub>] (Figure 15, middle) shows major distortions compared to the experimental x-ray structure. Thus, the force field is unsuccessful in simulating the stable monoclinic experimental crystal phase. The regular repeating pattern of the experimental structure is no longer visible, and thermal fluctuations are dramatic. As seen in the figure, the simulated crystal expands in the **a** direction by 15.8% and contracts in the **b** direction by 11.1%. Distortion in the perpendicular **c** direction is minor at 2.0%. Even the  $\beta$  angle increases by over 1° (1.3%). The nearly equal and opposite distortions in **a** and **b** axes allow the simulated density to remain in good agreement with the experimental density, being only 4.5% lower, an entirely fortuitous result. In the experimental structure from Figure 15, considerable free volume is observed, and upon closer inspection, the nitrate anions are stacked in eclipsed columns. However, upon simulation, the nitrates remain stacked, but in an irregular fashion, accompanied by a decrease in the free volume of the cell.

The simulated lattice for  $[(\text{CH}_3)_2\text{N}_2\text{H}_3][\text{NO}_3]$  (Figure 15, right) is in excellent agreement with the experimental orthorhombic x-ray structure. Aside from small thermal fluctuations, the simulated lattice retains its shape and symmetry relative to the crystal lattice. Deviations in the **a**, **b**, and **c** axes are +1.3%, +1.4%, and -3.6%, respectively. The cell angles were not allowed to vary from their 90° ideal values. The simulated density is only 1.0% lower than the experimental density.

Interestingly, the nitrate anions in the experimental lattices of  $[\text{N}_2\text{H}_5][\text{NO}_3]$  and  $[(\text{CH}_3)_2\text{N}_2\text{H}_3][\text{NO}_3]$  are not stacked in an apparent regular fashion as in  $[\text{CH}_3\text{N}_2\text{H}_4][\text{NO}_3]$ , but rather appear staggered. The simulated lattices of the former two crystals, coincidentally or not, show the smallest deviations from experiment, although in  $[\text{N}_2\text{H}_5][\text{NO}_3]$  some may argue that the deviations are important. Nonetheless, a possible reason for the unstable  $[\text{CH}_3\text{N}_2\text{H}_4][\text{NO}_3]$  simulated phase may be due to limitations in the nitrate force field, and the driving force to maximize hydrogen bonding interactions via irregularities in the stacking of the anion. Otherwise, the inability of the methylhydrazinium force field to perform well, considering the exceptional performance for the analogous neutral MEH, is inexplicable.

Figure 16 shows computed liquid densities and molar volumes for the three hydrazinium salts.

$[\text{N}_2\text{H}_5][\text{NO}_3]$	$[\text{CH}_3\text{N}_2\text{H}_4][\text{NO}_3]$	$[(\text{CH}_3)_2\text{N}_2\text{H}_3][\text{NO}_3]$ (unsymmetrical)			
M.P. (exp): 344 K	M.P. (exp): 313 K	M.P. (exp): 320 K			
Simulations of all three salts performed above melting points (348 K)					
$[\text{N}_2\text{H}_5][\text{NO}_3]$	$[\text{CH}_3\text{N}_2\text{H}_4][\text{NO}_3]$	$[(\text{CH}_3)_2\text{N}_2\text{H}_3][\text{NO}_3]$ (unsymmetrical)			
$\rho$ (g/cm <sup>3</sup> )	1.681	$\rho$ (g/cm <sup>3</sup> )	1.376	$\rho$ (g/cm <sup>3</sup> )	1.230
$V_M$ (cm <sup>3</sup> /mol)	56.55	$V_M$ (cm <sup>3</sup> /mol)	79.27	$V_M$ (cm <sup>3</sup> /mol)	100.12
(select H-bond distances labeled)					

Figure 16: Computed liquid densities and molar volumes for the hydrazinium salts, in addition to snapshots showing typical interactions between the cations and anions.

The liquids were simulated at 348 K, above the melting points of all three salts. All three have very high densities at the simulated temperature, decreasing from 1.681 g/cm<sup>3</sup> for  $[\text{N}_2\text{H}_5][\text{NO}_3]$  to 1.230 g/cm<sup>3</sup> for  $[(\text{CH}_3)_2\text{N}_2\text{H}_3][\text{NO}_3]$ . As the density decreases, the molar

volume increases down the hydrazinium series. The molar volume of  $[(\text{CH}_3)_2\text{N}_2\text{H}_3][\text{NO}_3]$  is nearly twice that of  $[\text{N}_2\text{H}_5][\text{NO}_3]$ . As shown below, the dynamics of these salts is sluggish, and we believe this is due in part to the strong hydrogen bonding that takes place between cations and the nitrate anions. Figure 16 shows snapshots from the simulations where such hydrogen bonding interactions can be observed.

The self-diffusion coefficients ( $D_s$ ) and rotational time constants were also evaluated for the cation and anion of each salt. In each salt, the anion exhibits faster translations dynamics than the cation (larger  $D_s$  values). Additionally,  $[\text{N}_2\text{H}_5][\text{NO}_3]$  exhibits faster dynamics overall relative to  $[\text{CH}_3\text{N}_2\text{H}_4][\text{NO}_3]$ , and  $[(\text{CH}_3)_2\text{N}_2\text{H}_3][\text{NO}_3]$ , and all are on the order of  $10^{-12} \text{ m}^2/\text{s}$ , although the 3 ns simulations may be inadequate to sample the diffusive regime, given the slow dynamics. Rotational time constants for the cations and anions of each IL are on the order of several hundred picoseconds.

The hydrazinium salt, 2-hydroxyethylhydrazinium nitrate (2-HEHN) is a low melting ionic liquid that has considerable potential for energetic applications. Although little experimental data is available in the literature, predictions were made concerning the physical and dynamical properties of this IL based on previous validation of the molecular force field. As shown in Figure 17, the liquid densities decrease linearly with increasing temperature. The experimental density at 298 K of  $1.42 \text{ g/cm}^3$  (Brand, A. J.; Drake, G.W. "Energetic hydrazinium salts." U.S. patent #6218577) is in excellent agreement with the simulated value of  $1.428 \text{ g/cm}^3$ . The liquid structure was evaluated via radial distribution analysis of the system components. The cation-cation, cation-anion, and anion-anion COM-COM radial distribution functions are shown in Figure 18. The attractive cation-anion (+-)  $g(r)$  is the most intense and occurs at the shortest distance of  $4 \text{ \AA}$ . A significant cation-anion longer range interaction occurs at  $\sim 9 \text{ \AA}$ . The repulsive cation-cation (++) and anion-anion (--) interactions are less intense and occur at longer distances of  $5.7 \text{ \AA}$  and  $7.3 \text{ \AA}$ , respectively. The two anion-anion peaks at shorter distance have intensity less than 1 and are not important. The cation-cation and anion-anion also show weaker correlations out at about  $12 \text{ \AA}$ .

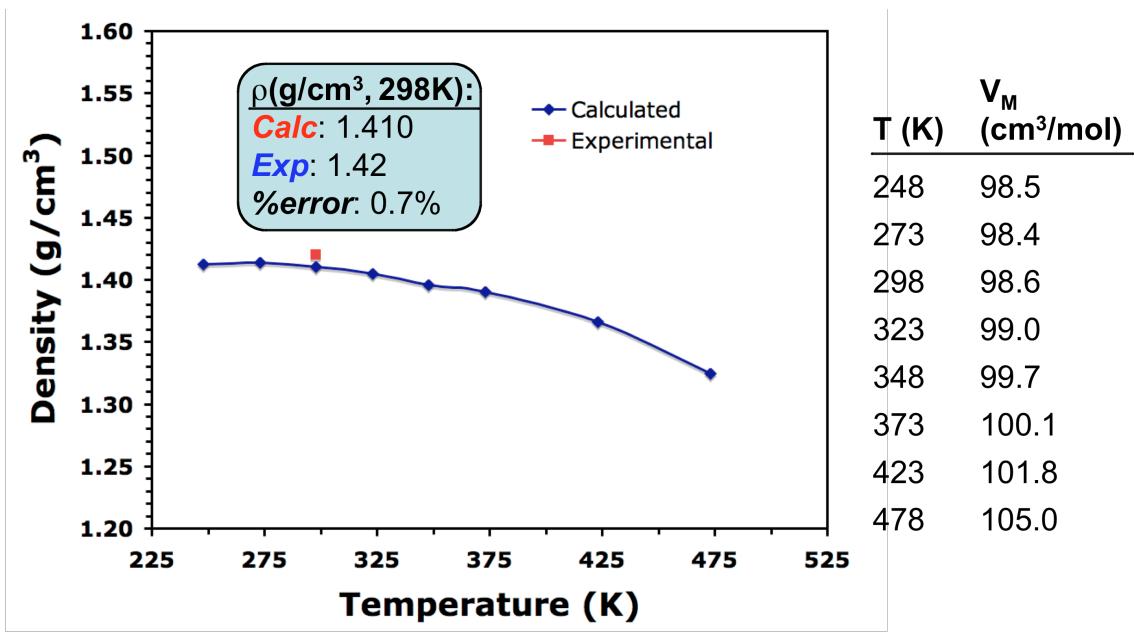


Figure 17: Computed density of hydroxyethylhydrazinium nitrate as a function of temperature.

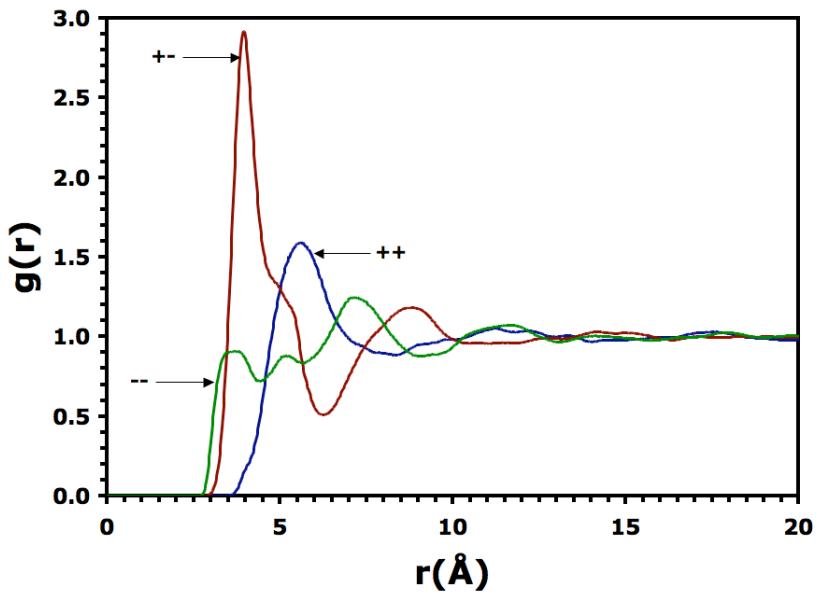
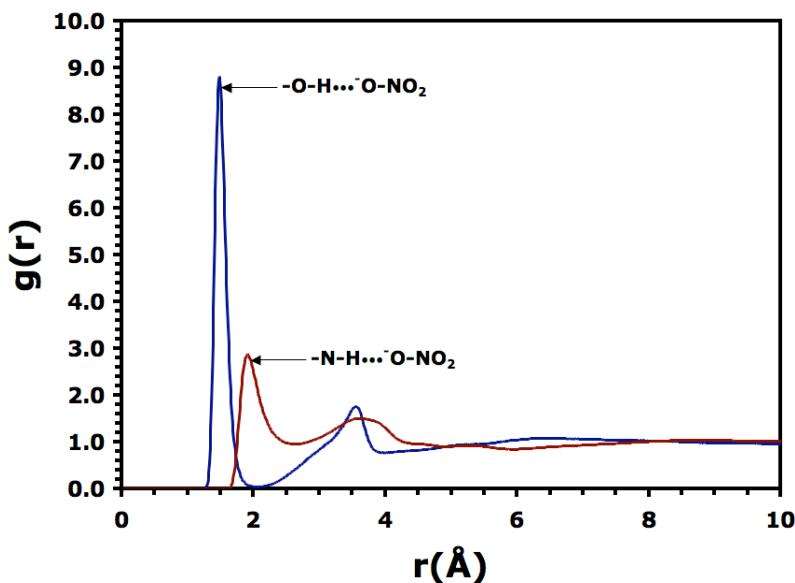


Figure 18: COM-COM radial distribution functions for cation/cation (++) , cation/anion (+-), and anion/anion (--) interactions in 2-HEHN.

The IL 2-HEHN is expected to exhibit strong hydrogen bonding in the liquid phase. As shown in Figure 19, the major hydrogen-bonding interactions between the cation and anion have been evaluated using a  $g(r)$  correlation. Here, the interaction between the nitrate oxygen atoms and either the hydroxyl hydrogen or amine hydrogens of 2- $\text{HEH}^+$  has been studied. The  $\text{N-H}\cdots\text{O}$  interaction is far weaker than the  $\text{O-H}\cdots\text{O}$  interaction. The former occurs at  $\sim 1.9$  Å while the latter occurs at the much shorter distance of  $\sim 1.5$  Å. The 1.5 Å hydrogen bond is very short relative to hydrogen bonds in general, and suggests that this interaction is very strong in the liquid. This is supported by the sharpness and intensity of the  $g(r)$  curve for this peak relative to the  $\text{N-H}\cdots\text{O}$  interaction. The correlations at about 3.5 to 4 Å are associated with the neighboring oxygens of the nitrate anion. The information provided by these  $g(r)$  curves is evidence of an IL that is dominated by hydrogen bonding due to the presence of many significant donor/acceptor sites.



*Figure 19: Site-site radial distribution functions for hydroxyl:nitrate interactions and amine:nitrate interactions in 2-HEHN.*

The dynamics of 2-HEHN were probed by calculating the MSD vs. time for the cation and anion, as well as their self-diffusion coefficients. The temperature dependence of the dynamics was evaluated over the temperature range of 223 to 473 K. Figure 20 shows the MSD ( $\text{\AA}^2$ ) vs. temperature (K) at four different observation times. Information about the melting/glass-transition region for an IL can be elucidated from the MSD vs. temperature curve in the region where the ions exhibit small fluctuations ( $<0.1 \text{ \AA}^2$ ), indicating lack of global motion. In Figure 20, the MSDs increase rapidly at higher temperature, making it difficult to establish behavioral characteristics at lower

temperatures. Thus, the breakout plots illustrate behavior over the entire temperature range focusing on smaller MSDs. As seen in the two figures for the cation and anion below about 250 K, motion over the 1000 ps observation range is  $<0.1 \text{ \AA}^2$ , indicating glassy behavior. However, above 250 K, displacements over the 1000 ps timeframe are greater than  $0.1 \text{ \AA}$  and mark the start of departure from linear behavior. Qualitatively, this is good agreement with the reported melting point of 2-HEHN of  $< 248 \text{ K}$ . Further studies of melting point using the PSPS method will allow quantitative confirmation.

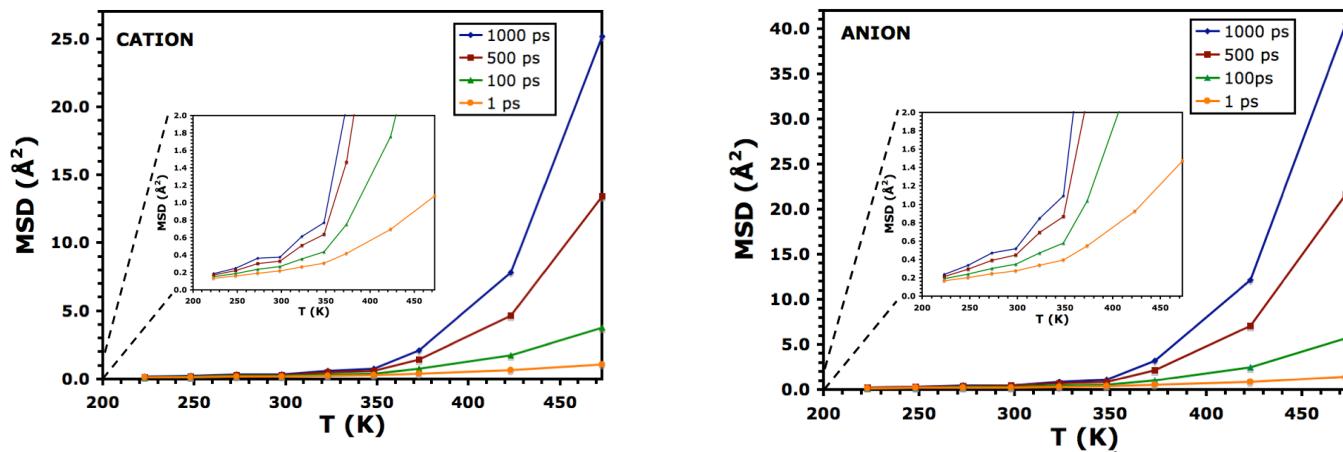


Figure 20: Simulated temperature dependence of 2-HEHN cation and anion MSDs ( $\text{\AA}^2$ ) at several elapsed times.

Self-diffusion coefficients were estimated from the MSD vs. time; at the lower temperatures, the cation and anion of 2-HEHN exhibit sub-diffusive behavior, making it impossible to quantitatively assign  $D_s$ . At low temperatures in the range of 223 to 348 K, the translational motion of the ions is very small, on the order of  $10^{-13} \text{ m}^2/\text{s}$ , much slower than previously reported ILs. This slow behavior is likely attributable to the strong hydrogen-bonding behavior of the IL. Although it is difficult to appraise these results in light of the lack of experimental evidence, it seems plausible that the slow dynamics may be due to hydrogen bonds that are too strong. At temperatures of 373 K and above, a speed-up in the dynamics is observed. At the highest temperature of 473 K, the MSDs are  $\sim 4 \times 10^{-11} \text{ m}^2/\text{s}$  and  $\sim 6 \times 10^{-11} \text{ m}^2/\text{s}$  for the cation and anion, respectively. The hydrogen bonds are labile this temperature region, allowing the species to move more freely in the bulk. Employing damped charges or using a polarizable may aid in the future study of these materials.

#### **4. Personnel Supported:**

This project represents a major element of Saivenkataraman Jayaraman's PhD thesis research. Dr. Jayaraman completed his thesis entitled "Computing thermodynamic and transport properties of Room Temperature Ionic Liquids and Molten Salts from Atomistic Simulations" in 2009, and is presently a postdoctoral researcher at Sandia National Laboratories. His thesis is available from UMI and the University of Notre Dame library. Other graduate students still at Notre Dame receiving partial support were Andrew Paluch and Pavi Tiruppathi. Mr. Paluch held an internship in the summer of 2009 at Sandia National Laboratories and Ms. Tiruppathi was a Space Scholar at Hanscom Air Force Base over the summer of 2010. Partial support was also provided to postdocs Wei Shi (currently at the National Energy Technology Laboratory), Manish Kelkar currently at DuPont), and Keith Gutowski (currently at BASF).

#### **5. Publications**

The following publications have benefited from either full or partial support from the project:

1. Manish S. Kelkar and Edward J. Maginn, "Calculating the Enthalpy of Vaporization of Ionic Liquid Clusters", *Journal of Physical Chemistry B.*, **2007**, 111, 9424-9427.
2. Daniel Strasser, Fabien Goulay, Manish S. Kelkar, Edward J. Maginn and Stephen R. Leone, "Photoelectron Spectrum of Isolated Ion-Pairs in Ionic Liquid Vapor", *Journal of Physical Chemistry A*, **2007**, 111, 3191-3195.
3. Manish S. Kelkar and Edward J. Maginn, "Effect of Temperature and Water Content on the Shear Viscosity of the Ionic Liquid 1-ethyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide As Studied by Atomistic Simulations", *Journal of Physical Chemistry B*, **2007**, 111, 4867-4876.
4. Wei Shi and Edward J. Maginn, "Continuous Fractional Component Monte Carlo: An Adaptive Biasing Method for Open System Atomistic Simulations", *Journal of Chemical Theory and Computation*, **2007**, 3, 1451-1463.
5. Edward J. Maginn, "Atomistic Simulation of the Thermodynamic and Transport Properties of Ionic Liquids", invited article for *Accounts of Chemical Research*, **2007**, 40, 1200-1207.
6. Saivenkataraman Jayaraman and Edward J. Maginn, "Computing the Melting Point and Thermodynamic Stability of the Orthorhombic and Monoclinic Polymorphs of the Ionic Liquid 1-n-Butyl-3-methylimidazolium Chloride", *Journal of Chemical Physics*, **2007**, 127, 214504.

7. Wei Shi and Edward J. Maginn, “Atomistic Simulation of the Absorption of Water in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ([hmim][Tf<sub>2</sub>N])”, *Journal of Physical Chemistry B*, **2008**, 112, 2045-2055.
8. Wei Shi and Edward J. Maginn, “Improvement in Molecule Exchange Efficiency in Gibbs Ensemble Monte Carlo: Development and Implementation of the Continuous Fractional Component Move”, *Journal of Computational Chemistry*, **2008**, 29, 2520-2530.
9. Wei Shi and Edward J. Maginn, “Atomistic Simulation of the Absorption of Carbon Dioxide and Water in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ([hmim][Tf<sub>2</sub>N])”, *Journal of Physical Chemistry B*, **2008**, 112, 2045-2055.
10. Manish S. Kelkar, Wei Shi and Edward J. Maginn, “Determining the Accuracy of Classical Force Fields for Ionic Liquids: Atomistic Simulation of the Thermodynamic and Transport Properties of 1-Ethyl-3-methylimidazolium Ethylsulfate ([emim][EtSO<sub>4</sub>]) and Its Mixtures with Water”, *Industrial and Engineering Chemistry Research*, **2008**, 47, 9115-9126.
11. Keith E. Gutowski, Burcu Gurkan and Edward J. Maginn, “Force Field for the Atomistic Simulation of the Properties of Hydrazine, Organic Hydrazine Derivatives, and Energetic Hydrazinium Ionic Liquids”, *Pure and Applied Chemistry*, **2009**, 81, 1799-1828.
12. Jason Baxter, Zhixi Bian, Gang Chen, David Danielson, Mildred S. Dresselhaus, Andrei G. Fedorov, Timothy S. Fisher, Christopher W. Jones, Edward Maginn, Uwe Kortshagen, Arumugam Manthiram, Arthur Nozik, Debra Rolison, Timothy Sands, Li Shi, David Sholl, Yiying Wu, “Nanoscale Design to Enable the Revolution in Renewable Energy”, *Energy and Environmental Science*, **2009**, 2, 559-588.
13. Amrish Menjoge, JaNeille Dixon, Joan Brennecke, Edward Maginn and Sergey Vasenkov, “Influence of Water on Diffusion in Imidazolium-Based Ionic Liquids: A Pulsed Field Gradient NMR Study”, *Journal of Physical Chemistry B*, **2009**, 113, 6353-6359.
14. Edward J. Maginn “From Discovery to Data: What Must Happen for Molecular Simulation to Become a Mainstream Chemical Engineering Tool”, invited ‘Perspectives’ article, *AICHE Journal*, **2009**, 55, 1304-1310.
15. Edward J. Maginn, “Transforming Molecular Simulation into a Mainstream Chemical Engineering Tool”, *Chemical Engineering Progress*, **2009**, 105, 12.
16. Edward J. Maginn, “Molecular Simulation of Ionic Liquids: Current Status and Future Opportunities”, Invited review, *Journal of Physics: Condensed Matter*, **2009**, 21, 373101.

17. Saivenkataraman Jayaraman, Aidan P. Thompson, Anatole von Lilienfeld, and Edward J. Maginn, "Molecular Simulation of the Thermal and Transport Properties of Three Alkali Nitrate Salts", *Industrial and Engineering Chemistry Research*, **2010**, 49, 559-571.
18. Andrew S. Paluch, Saivenkataraman Jayaraman, Jindal K. Shah, and Edward J. Maginn, "A Method for Computing the Solubility Limit of Solids: Application to Sodium Chloride in Water and Alcohols", *Journal of Chemical Physics*, in press.

## **6. Interactions/Transitions:**

### **Invited Talks Referencing This Work**

1. "Using Atomistic Simulations to Understand Structure-Property Relationships: Application to Ionic Liquids and Crystalline Nanoporous Materials", Chemical and Biological Engineering seminar, University of Colorado, Boulder, CO, March 13, **2007**.
2. "Using Atomistic Simulations to Understand Structure-Property Relationships: Application to Ionic Liquids and Crystalline Nanoporous Materials", Chemical and Biological Engineering seminar, Northwestern University, Evanston, IL, March 29, **2007**.
3. "Can Classical Simulations Really Predict Properties of Ionic Liquids? On the Pitfalls and Success Stories of Modeling Ionic Liquids", Structures and Dynamics of Ionic Liquids conference, Kazusa Akademia Park, Chiba, Japan, August 3, **2007**.
4. "Using Atomistic Simulations to Predict the Thermodynamic and Transport Properties of Ionic Liquids", Second International Congress on Ionic Liquids, Yokohama, Japan, August 7, **2007**.
5. "Development and Use of Atomistic Simulation Methods to Understand Structure-Property Relationships for Ionic Liquids", Department of Chemical Engineering Colloquium, Rice University, Oct. 18, **2007**.
6. "Development of new post-combustion carbon dioxide capture solvents: Are ionic liquids the answer?" American Chemical Society meeting, New Orleans, LA, April 7, **2008**.
7. "Development and application of advanced molecular simulation methods for computing the properties of ionic liquids", American Institute of Chemical Engineers Spring Meeting, New Orleans, LA, April 8, **2008**.
8. "Development and Use of Atomistic Simulation Methods to Understand Structure-Property Relationships for Ionic Liquids", Department of Chemical, Biological and Materials Engineering, University of Oklahoma, April 24, **2008**.
9. "On the Use of Atomistic Simulations to Understand and Predict the Thermodynamic

Properties of Ionic Liquids" (Plenary Lecture), 20th International Conference on Chemical Thermodynamics, Warsaw, Poland, Aug. 3-8, **2008**.

10. "Carbon Dioxide Capture from Flue Gas Using Ionic Liquids: A Combined Molecular Modeling and Experimental Study" (Keynote Speaker), ASME 3rd Energy Nanotechnology International Conference, Jacksonville, FL, Aug. 10-14, **2008**.
11. "Molecular Modeling as a Tool for Relating Properties of Ionic Liquids to Chemical Structure", 214<sup>th</sup> Electrochemical Society Meeting, Honolulu, Hawaii, October 12, **2008**.
12. "Progress and Outlook for Molecular Dynamics Simulations", AIChE Centennial Session on Molecular Modeling, AIChE meeting, November 18, **2008**.
13. "Using Molecular Simulations to Design New Ionic Liquids for Use in Energy and Propulsion Applications", University of Florida Chemical Engineering departmental seminar, February 3, **2009**.
14. "On the Use of Molecular Simulations for Computing Thermodynamic and Transport Properties of Ionic Liquids", Centre European de Calcul Atomique et Moleculaire workshop, Dublin, Ireland, April 6, **2009**.
15. "Using Molecular Simulations to Design New Ionic Liquids for Use in Energy and Propulsion Applications", Department of Chemistry seminar, University of New Orleans, New Orleans, LA, April 17, **2009**.
16. "On the Use of Monte Carlo and Molecular Dynamics to Probe the Properties of Ionic Liquids", Air Force Office of Scientific Research Molecular Dynamics Contractors' Meeting, San Diego, CA, May 17, **2009**.
17. "Molecular Modeling of Solubility in Ionic Liquids", 8<sup>th</sup> World Congress on Chemical Engineering, Montreal, Quebec, Canada, August, **2009**.
18. "Understanding Sorption and Diffusion in Ionic Liquids Via Molecular Simulation", Fakultät für Chemie und Mineralogie, Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Leipzig, Germany, Nov. 30, 2009.
19. "On the Use of Molecular Simulations to Compute Ionic Liquid Phase Behavior", Winter School on Ionic Liquids, Warnemünde, Germany, Dec. 3, **2009**.
20. "Molecular Simulation Methods for Computing Thermodynamic and Transport Properties of Ionic Liquids and Molten Salts", Eduard-Zintl-Institut für Anorganische und Physikalische Chemie Technische Universität Darmstadt, Darmstadt, Germany, Dec. 7, **2009**.

## Contributed Talks Referencing This Work

1. Joan Brennecke, Jessica L. Anderson, JaNeille K. Dixon, and Edward J. Maginn “Ionic Liquids for Post-Combustion CO<sub>2</sub> Capture”, AIChE Spring meeting, Houston, TX, April 2007.
2. Saivekataraman Jayaraman and Edward J. Maginn, “Computing the Melting Point of Ionic Liquids from Atomistic Simulations”, Midwest Thermodynamics and Statistical Mechanics Conference, Iowa State University, June 7<sup>th</sup>, 2007.
3. Jessica Anderson, JaNeille K. Dixon, Mark. J. Muldoon, J. F. Brenecke and Edward J. Maginn, “Ionic liquids as CO capture media”, CHEMRAWN-XVII and ICCDU-IX Conference on Greenhouse Gases, Mitigation and Utilization, Kingston, Ontario, Canada, July 11, 2007.
4. Amrish R. Menjoge, JaNeille K. Dixon, Joan F. Brennekce, Edward J. Maginn, and Sergey Vasenkov, “Influence of Water on Diffusion in Ionic Liquids: Pulsed Field Gradient NMR Study”, AIChE Annual Meeting, Salt Lake City, UT, Nov. 2007.
5. Sai Jayaraman and Edward J. Maginn, “Computing the Melting Point of Ionic Liquids from Atomistic Simulations”, AIChE Annual Meeting, Salt Lake City, UT, Nov. 2007.
6. Wei Shi and Edward J. Maginn, “Continuous Fractional Component Monte Carlo: The General Biased Slow-Growth Method for Phase Equilibrium Simulations”, AIChE Annual Meeting, Salt Lake City, UT, Nov. 2007.
7. Jessica L. Anderson, JaNeille K. Dixon, Wei Shi, Kate E. Wilbanks, Edward J. Maginn and Joan F. Brennecke, “Ionic Liquids as Absorption Media for Mixed Gas Capture”, AIChE Annual Meeting, Salt Lake City, UT, Nov. 2007.
8. Edward J. Maginn, JaNeille K. Dixon, Elaine Mindrup, Wei Shi, Joan F. Brennecke, and William F. Schneider, “Evaluation of Ionic Liquids as Novel Post-Combustion Carbon Dioxide Capture Solvents”, American Institute of Chemical Engineers Spring Meeting, New Orlean, LA, April 8, 2008.
9. Edward J. Maginn, “Evaluation of Ionic Liquids in Post-Combustion CO<sub>2</sub> Capture”, Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 6, 2008.
10. Edward J. Maginn, Wei Shi, Keith Gutowski, Manish Kelkar and Saivenkataraman Jayaraman, “Development and Use of Atomistic Simulations to Understand Structure-Property Relationships for Ionic Liquids”, Air Force Office of Scientific Research Contractors Meeting, Vienna, VA, May 20, 2008.
11. Jindal Shah and Edward J. Maginn, “Novel Monte Carlo Algorithm to Sample

Intramolecular Degrees of Freedom of Linear, Branched and Cyclic Molecules with Fixed Bond Length Constraints”, AIChE Annual Meeting, Philadelphia, PA, November 19, **2008**.

12. Manish S. Kelkar and Edward J. Maginn, “On the Use of Molecular Modeling to Predict a Wide Range of Thermodynamic and Transport Properties of the Ionic Liquid 1-Ethyl-3-Methylimidazolium Ethylsulfate and Its Mixtures with Water”, AIChE Annual Meeting, Philadelphia, PA, November 19, **2008**.
13. Manish S. Kelkar, Mark B. Shiflett, Akimichi Yokozeki and Edward J. Maginn, “Atomistic Simulation Study of Hydrofluorocarbon-Ionic Liquids Mixtures”, AIChE Annual Meeting, Philadelphia, PA, November 19, **2008**.
14. Andrew Paluch, Sai Jayaraman, Jindal Shah and Edward J. Maginn, “An Adaptable Method to Calculate the Solubility Limit of Solids by Molecular Simulation”, AIChE Annual Meeting, Nashville, TN, November 9, **2009**

### **Collaborations**

We have collaborated with Prof. Stephen Leone at UC Berkeley / LBNL and published one paper. We have also collaborated with AFOSR grantees Mark Gordon (Iowa State / Ames Lab), Greg Voth (Utah), Robin Rogers (Alabama) and Yu-Hui Chiu (Hanscom Air Force Base).

### **Honors and Awards**

Inaugural Early Career Award, sponsored by the Computational Molecular Science and Engineering Forum of the American Institute of Chemical Engineers, November, 2009.

Runner up (with J. I. Siepmann), 4th Industrial Fluid Properties Simulation Collective competition, 2008.

Runner up and Best Overall Entry (with J. I. Siepmann), 3<sup>rd</sup> Industrial Fluid Properties Simulation Collective competition, Molecular Transferability and State Conditions Transferability categories, 2007.

BP College of Engineering Outstanding Teacher Award, University of Notre Dame, 2006.